

Time-Resolved Pyrolysis Mass Spectrometry of Coal: A New Tool for
Mechanistic and Kinetic Studies

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INTRODUCTION

Most coal devolatilization studies so far have focussed on the determination of reaction rates for reactions occurring under widely different conditions encountered in liquefaction, gasification, coking or combustion processes. Published rates on more or less comparable coals may differ by several orders of magnitude, especially when obtained at high temperatures (>1000 K) and/or high heating rates (10^2 - 10^5 K/s) (1,2).

At the present state-of-the-art in coal devolatilization research, more emphasis should perhaps be placed on elucidating the mechanisms of the chemical reactions underlying the observed phenomena. When studying thermal conversion reactions in coal it seems correct to concentrate first on the so-called "primary" reactions before attempting to elucidate the many possible secondary reaction pathways. This is especially true since most secondary reaction pathways are strongly influenced by reactor design and experimental conditions.

The devolatilization behavior of coal will be determined primarily by the chemical composition of coal and secondly by the experimental conditions. Under properly designed vacuum micropyrolysis experiments working with sufficiently small particles (<50 μ diameter), it is possible to avoid mass and heat transport limitations (3) and minimize the secondary reactions. Using premium coal samples from Argonne National Laboratory (4) the chemical composition can be well defined and possibly characterized by major factors such as rank and depositional environment (5). Recent advances in pyrolysis mass spectrometry (Py-MS), viz, time-resolved Py-MS (TR Py-MS), along with multivariate analysis techniques enable extraction of underlying chemical components (6) from a single experiment; thus reducing the uncertainty due to varying reactions conditions in different experiments. This paper demonstrates the feasibility of obtaining valuable mechanistic and kinetic data using microgram amounts of carefully selected coal samples under properly designed reaction conditions using TR Py-MS techniques in combination with advanced multivariate data analysis methods.

EXPERIMENTAL

A sample of hvAb Pittsburgh #8 coal was picked up in large chunks from the mine mouth and subsequently ground and sieved under nitrogen. Ultimate and proximate analysis data are shown in Table I. Sample preparation was discussed earlier (7) in detail.

(Time-Resolved Pyrolysis Mass Spectrometry)

Time-resolved Py-MS analyses were done under the following conditions: Curie-point temperature 610°C , temperature-rise time 5.4 s, total heating time 10 s, electron energy 12 eV, mass range scanned 50 to 200 amu, scanning speed 1000 amu/s, number of scans 41, total scan time 8 s. Each spectrum scanned was stored separately in the IBM 9000 computer.

(Multivariate Data Analysis)

In order to give all the variables an equal contribution, and for reasons explained by Malinowski (8), factor analysis was done on the "correlation around the origin" matrix. For this study, the number of factors used was selected by determining the leveling off of the slope (8) and the ratio of the eigenvalue (9). Deconvolution of the components was performed by using a combination of "pure mass" (8,10) and "variance diagram" (VARDIA) (6) techniques.

(Kinetic Analyses)

Kinetic analysis was based on the total ion current plot. The assumption was made that each maximum in the bimodal curve reflects a single rate process and that a first order rate equation describes the process. The parameters computed based on the maximum rate of generation at the peak of the curve are listed in Table I. The distributed activated energy model (11) was used as an alternative approach.

RESULTS AND DISCUSSION

The time-resolved total ion current (TIC) profile of the Pittsburgh #8 coal sample is shown in Figure 1b. The TIC profile has a distinctly bimodal character with a pronounced low temperature maximum near 370°C and a larger, high temperature maximum near 560°C. These temperatures, estimated from the temperature/time profile of the blank Curie-point pyrolysis filament (shown in Figure 1a) are believed to be accurate within 5%. The time-integrated spectrum of the coal sample, shown in Figure 2, shows that the most abundant homologous ion series in the pyrolysis mass spectra of fresh whole coals are the "phenols". Other major components dominating the spectra are the "benzenes", "naphthalenes" and the short chain aliphatic hydrocarbons. This matches with the results from this laboratory obtained on 102 Rocky Mountain coals (5).

Using the multivariate data analysis procedures, mentioned before, the evolution profiles of the components (separate groups of correlated mass peaks) were obtained. These profiles, labeled A, B, C and D are shown in Figure 1c. The corresponding numerically extracted spectra showing the composition of each component along with the total variance percentage are shown in Figure 3a, b, c and d.

The low temperature component A appears to represent a vacuum distillable oil consisting largely of aromatic hydrocarbon series ("benzenes", "naphthalenes" and "biphenyls/acenaphthenes"). Bench scale vacuum extraction studies of a hvBb Hiawatha coal showed the naphthene rich distillable fraction to represent approx. 4% of the fresh coal (12). It is now rather widely accepted that coal deposits go through an "oil formation window" during their coalification history in a similar manner observed for oil shale deposits. Maximum oil generation is likely to occur in coals of high volatile bituminous rank. Interestingly, in our experience this component is not readily observed under typical thermal analysis conditions.

Components B, C, and D together make up the main pyrolysis event in Figure 1b. Component B appears at a somewhat lower temperature than components C and D. The near symmetrical shape of the intensity profiles of components B and C indicates a depolymerization (such as found in thermoplastic materials) degradation behavior leading to rapid, complete pyrolysis without major charring tendencies. Component D, however, behaves more like a crosslinking substance (such as found in thermoplastic materials) with a wider temperature profile and a slow, high temperature tail indicating incomplete pyrolysis, presumably accompanied by char formation.

Which structural moieties, if any, are represented by components B, C and D? Identification of component D is relatively straightforward. As shown in Figure 3d, this component is dominated by a strong series of alkyl substituted phenols and resembles the Py-MS patterns of pure vitrinites (13) and fossil wood (14) samples.

Highly similar patterns have been observed in numerically extracted component spectra of various coal data sets obtained by Py-MS (15). Consequently, component D appears to represent the abundant vitrinite macerals present in the Pittsburgh #8 coal sample.

Component B is the early component in the "depolymerization" region (see later) and is characterized by branched or alicyclic hydrocarbons. This component is also characterized by a prominent ion series at m/z 60, 74, 88, 102, etc. (most prominent in the corresponding loading spectra, not shown here), as marked by stars in Figure 3b and thought to represent short chain fatty acids. Patterns similar to Figure 3b can be observed in Messel shale (16) as well as in sporinite concentrates (13) and may represent liptinitic structural moieties present in several different coal macerals.

The numerically extracted spectrum of component C (Figure 3c) reveals an entirely different chemical structure consisting nearly exclusively of aliphatic hydrocarbon moieties. On the basis of previously reported Py-MS studies of model compounds and maceral concentrates (13), this component is believed to consist primarily of straight chain alkanes, alkenes and alkadienes. Under the low voltage electron ionization conditions used in this experiment, short chain alkanes (C_{15}) produce mainly the alkene and alkadiene molecular ion series as well as various fragment ion series, which are visible in Figure 3c. Mixtures of straight chain aliphatic hydrocarbons such as seen in Figure 3c are typical of the pyrolyzates of polyethylene-like structures such as found under vacuum micropyrolysis conditions in liptinitic macerals derived from fossil plant cuticles (17) and/or algal materials (16).

It should be mentioned, however, that by selecting a limited mass range (m/z 50-200) many important small molecules (e.g., CH_4 , NH_3 , H_2O , HCN , CO , CH_2O , CH_3OH , H_2S , HCl , CO_2 and various C_2 compounds) are ignored in addition to many large organic molecules. This limits the characterization of the char forming process, as well as making it hard to compare our data with the data of other workers on the kinetics of evolution of small molecules (18, 19).

In spite of these limitations, the data obtained on the kinetic parameters seem to match very well with our understanding of the events marked by the two distinct humps in Figure 1b. The activation energy of 10 Kcal mol^{-1} is reasonable to expect for the thermophysical kinetics related to "desorption" of the mobile phase. The latter value of 62 Kcal mol^{-1} , which also matches with the value calculated using the distributed activation energy model, is expected for thermochemical kinetics for breaking of ethylene bridges between aromatic rings and agrees well with reported values for this step (2).

The observation of three different types of thermal behavior, as judged from the shape of the deconvoluted components, namely "desorption" (vacuum distillable component A), "depolymerization" (thermoplastic components B and C), and "thermal degradation" (thermosetting component D) points to the need for a kinetic model with at least three different reaction order terms. The desorption process is likely to have a reaction order between 0 and 1. The thermosetting (char formation) terms, on the contrary, would be expected to exhibit reaction orders substantially greater than 1. Only the two thermoplastic components (B and C) should follow first order unimolecular decomposition pathways under our vacuum micropyrolysis conditions. We are working on the development of a devolatilization model based on these TR Py-MS observations. In principle, this methodology can be applied to the "pure" maceral constituents of coal. Once the kinetic models for each maceral type are well established, a useful devolatilization model for the "mixture" coal might be within reach. In conclusion, computer-assisted TR Py-MS techniques enable deconvolution of chemical components, thereby allowing more insight into the chemistry of coal devolatilization.

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TABLE I

ANALYSIS OF COAL

	C	H	N	S	O	H/C	BTU/lb
Ultimate Analysis (DAF)	83.75	5.46	1.56	2.15	7.08	0.78	13,976
Proximate (as rec'd)	Moisture		Ash		Volatile Matter		
	0.57		7.27		37.86		

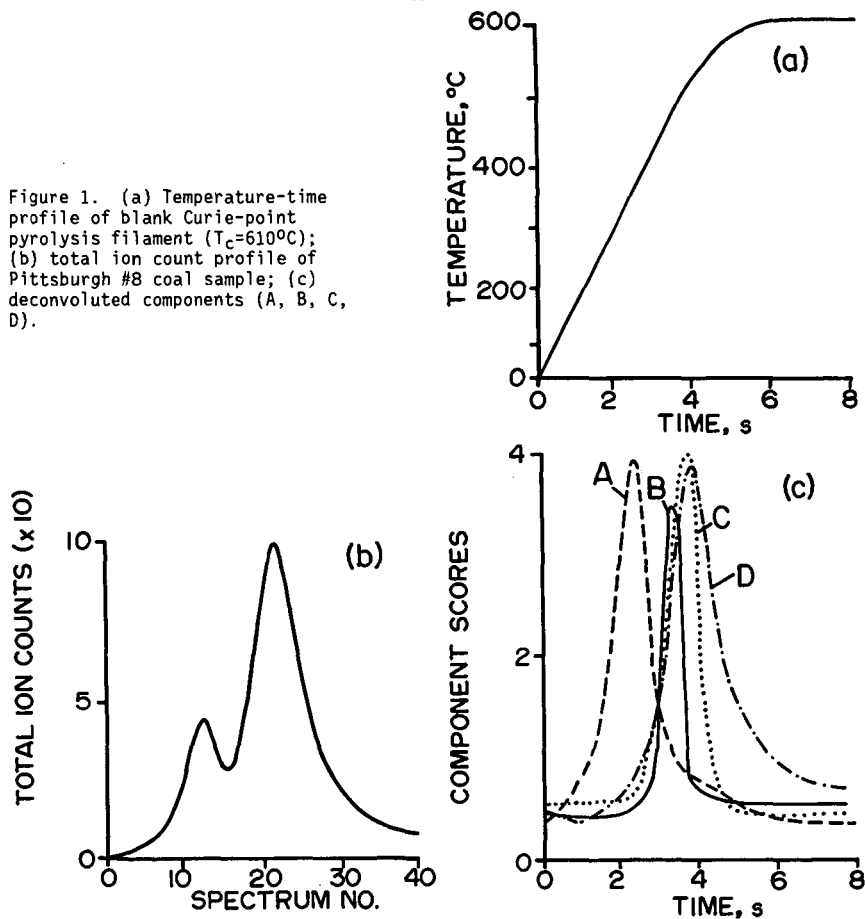
TABLE II
KINETIC PARAMETERS CALCULATED FROM TIME-RESOLVED PY-MS DATA

	Thermal Extraction Step	Bulk Pyrolysis Step
Energy of Activation, Kcal mol ⁻¹	10	62(60)*
Frequency Factor, s ⁻¹	10 ⁵	10 ¹² (10 ¹³ **)

* reference (2)

** Distributed Activation Energy Model

Figure 1. (a) Temperature-time profile of blank Curie-point pyrolysis filament ($T_c=610^\circ\text{C}$); (b) total ion count profile of Pittsburgh #8 coal sample; (c) deconvoluted components (A, B, C, D).



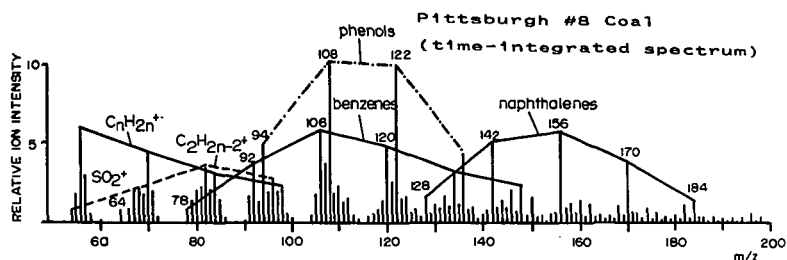


Figure 2. Time-integrated spectrum obtained by summing all 41 spectra recorded during time-resolved pyrolysis MS run. Note dominant series of homologous molecular ions characteristic of rank (hvAB) as well as of depositional environment and weathering status. Compare with deconvoluted spectra in Figure 3.

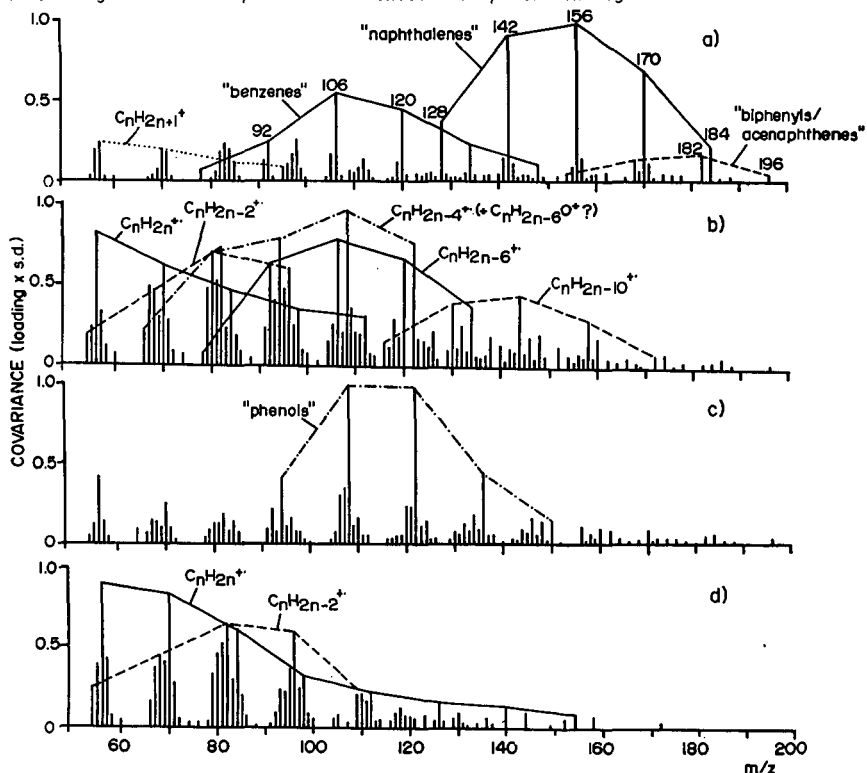


Figure 3. Numerically extracted ("deconvoluted") spectra of the four components shown in Figure 1. Note differences in % variance represented (summed variance of the four components is 99% of the total variance in all 41 spectra).